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1 Relationship between chemical and mechanical degradation of 2 aged paper: fibre versus fibre-fibre bonds

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16
17 **Abstract** Paper is susceptible to chemical degradation through hydrolysis and oxidation, resulting in
18 embrittlement and failure. Understanding the embrittlement process is important to ensure the preservation and
19 longevity of historical paper-based documents. However, the complex and architected paper microstructure is a
20 major challenge for fully understanding this process. Two papers with different microstructures were artificially
21 aged under hydrolytic and oxidative exposure conditions, and the consequences of ageing were studied. The fibre
22 embrittlement, the fibre-fibre bonds deterioration, and the evolution of paper microstructure upon ageing are
23 evaluated through macroscopic and localised mechanical tests, as well as through morphological observations at
24 the microscopic scale. It was concluded, from the different tests in the two principal orientations of the paper, that
25 fibre embrittlement plays a more significant role in the embrittlement process than fibre-fibre bonds deterioration.

26 Specifically, the cellulose chain scissions led to fibre embrittlement, irrespective of the oxidative or hydrolytic
27 nature of the chemical degradation mechanism. Furthermore, we identify a critical degree of polymerisation for
28 cellulose ($DP_c \sim 750$) below which the evolution of mechanical properties accelerates significantly, regardless of
29 the type of mechanical testing performed. Fibre analysis suggests that the decline in fibre resistance results in
30 fractures occurring under stress at weak points of the fibres, such as kinks or twists.

31 **Keywords** Hydrolysis, Oxidation, Microstructure, Morphology, Tensile testing, Fibre orientation.

32 **1 Introduction**

33 Paper embrittlement is a major concern for the preservation of books and documents. Among the various aspects
34 of paper ageing, mechanical resistance is of prime importance because it can seriously impede handling and
35 reading. To address this issue, papers can be treated via a polymer network reinforcement, or lined on a more
36 resistant paper substrate (Piovesan et al. 2018; Ferrandin-Schoffel et al. 2023). Permanent paper, which contains
37 an alkaline reserve to slow down its ageing, can be used for long-term preservation and archival purposes (Frase
38 1997). However, understanding the consequences of degradation on the mechanical behaviour of paper, and more
39 specifically the role of the fibres and fibre-fibre bonds in the embrittlement process, can help to better formulate
40 the papers and the treatments with the aim of improving durability. The objective of this study is to provide further
41 insight into the correlation between chemical and mechanical ageing of paper, in order to understand how the
42 chemical degradation under different ageing conditions affects its mechanical properties. In this regard, two papers
43 with different microstructures were studied.

44 Paper is a structured material made from plant fibres, usually from wood, bast fibres plants or cotton. During the
45 manufacturing process, the fibres are separated from each other by chemical and mechanical treatments, suspended
46 in water, then dried in the shape of sheets (Young and Rowell 1986; Neimo 1999). The papermaking machine
47 induces an orientation of the fibres in the sheet, conferring to the paper an anisotropic mechanical behaviour. The
48 fibres are entangled and adhere to each other through fibre-fibre bonds. These bonds consist on different adhesion
49 phenomena: weak bonds such as Coulomb forces, Van der Waals forces and hydrogen bonds, and molecular
50 interdiffusion between the swollen fibres in contact, mechanical entanglement of the fibrils on the surface of the
51 fibres (Hirn and Schennach 2015). These fibrils are produced by the refining process in order to increase the
52 contact surface and the mechanical entanglement, and therefore the adhesion between fibres (Sampson and Wang
53 2020). Moreover, the manufacturing process can induce defects along the fibre, such as kinks, or twists (Aslan et
54 al. 2011; Ali 2012; Ciesielski et al. 2019; Richely et al. 2022). The characteristics of the fibres, including their

55 nature, length and diameter, as well as the density of the sheets and the degree of refining are parameters that can
56 vary from one paper to another, and that can have a strong impact on the mechanical properties (Iribarne and
57 Schroeder 2000; l'Anson et al. 2006; Kontturi et al. 2021). These parameters should be monitored in order to
58 reveal the relevant physical parameters that govern the changes in the mechanical behaviour upon chemical
59 degradation.

60 Paper also contains other plant fibre structures, especially fibres' fragments of small size called fines, defined as
61 the fraction of the pulp stock that will pass a round hole 76 μm in diameter (TAPPI standard method T 261 cm-
62 00). They will be considered in this study, as they can have an impact on the mechanical strength of paper. Printing
63 paper also contains additives, such as fillers and surface treatment products (Henniges et al. 2016), that can also
64 impact mechanical behaviour.

65 However, the mechanical strength of paper is mostly determined by its structure, e.g., a random network of
66 entangled fibres. The density of the network is responsible for contacts between fibres (Sampson 2001, 2009).
67 They adhere to each other through deformable fibre-fibre bond (Iribarne and Schroeder 2000; Barbier et al. 2009)
68 thanks to the phenomena described hereabove. The mechanical properties of paper are thus due to the strength of
69 individual fibres, of fibre-fibre bonds, and to the entanglement between fibres.

70 Macroscopic mechanical properties can be obtained through tests such as compression, tensile tests or fatigue tests,
71 which give information on the visco-elastoplastic behaviour of paper with damage (Haslach, Jr. 2000). Due to the
72 orientation of the fibres in the sheet, these properties are determined in the two principal axes of the sheet (Kurei
73 et al. 2022). However, to have access to the strength of individual fibres and fibre-fibre bonds, specific tests can
74 be used, as for example tensile tests on unique fibres or adhesion tests on unique fibre-fibre bonds (Schmied et al.
75 2012; Yue et al. 2019; Maraghechi et al. 2023). Obtaining individual fibres behaviour is challenging, especially
76 because papers include a wide range of fibres dimensions. Moreover, it may not accurately mirror the actual stress
77 within a paper under tensile test. Therefore, *in-situ* characterisation is necessary, and localised tests can be used.
78 For example, the zero-span tensile test consists of pulling a paper strip with no gap between the jaws. It is
79 considered that the pulling is exerted only on the fibres without loading the network (Gurnagul and Page 1989;
80 Wathén et al. 2005; Batchelor et al. 2006). Similarly, water-saturated tensile test involves immersing the paper in
81 water prior to testing, which results in the weakening of fibre-fibre bonds and favours fibre slippage.

82 Another approach consists in varying the structural parameters of paper and measure their impact on macroscopic
83 properties to determine the contributions of fibre and fibre-fibre bonds resistance on the mechanical strength of

84 paper (Marulier et al. 2015; Deogekar et al. 2019). Authors have studied the morphology of fibres by cutting them
85 before the papermaking process, as well as the strength of bonding through refining or adjoining additives to the
86 pulp (l'Anson et al. 2006). The impact of fibres morphology has been correlated to the mechanical properties in a
87 semi-empirical equation introduced by Page (Page 1969) (**equation 1**). In particular, this equation links tensile
88 and zero-span tensile strength to the length of fibres and to the bonding areas. Such microstructure parameters can
89 be obtained through microscopic observations or X-ray microtomography (Peyrega et al. 2009; Bache-Wiig and
90 Henden 2010; Wernersson et al. 2014; Emerson et al. 2017). However, quantification from such images can be
91 difficult due to insufficient resolution leading to incomplete fibre identification, especially for dense papers. The
92 wide range of available tests and their limitations highlight the need for a comprehensive study at the different
93 length scales.

94 Cellulose being the main polymer that composes paper fibres, its degree of polymerisation (DP) is a key parameter
95 to be monitored during the ageing of paper. The chemical degradation under archival conservation conditions is
96 mainly due to the hydrolysis of cellulose (Gehlen 2010; SriBala and Vinu 2014). However, for permanent papers,
97 the kinetics of the acid-catalysed hydrolysis being slowed down by an alkaline reserve, the oxidation of cellulose
98 cannot be neglected (Nevell and Zeronian 1985; Margutti et al. 2001; Potthast et al. 2006). These two degradation
99 mechanisms have several impacts on paper, including cellulose chain scissions and a change in cellulose
100 crystallinity, consequently affecting paper water content (Haas et al. 1967; Gehlen 2010; Driemeier et al. 2012).

101 In the literature, the impact of chemical ageing on the mechanical strength of paper has been evaluated mostly
102 through tensile and zero-span tensile tests (dry and wet) and folding endurance tests (Emsley et al. 1997; Zervos
103 and Moropoulou 2005; Carrascal et al. 2018; Kurei et al. 2022). A significant reduction in folding endurance as
104 well as an embrittlement of paper is observed in both artificially and naturally aged paper (Wilson et al. 1955;
105 Barrow and Sproull 1959; Horst et al. 2020). Based on Page's equation, Zou concluded that acid cotton paper
106 embrittlement under accelerated ageing was due to a decrease of fibre strength (Zou et al. 1994). Kaminska
107 demonstrated that the relationship between the number of cellulose chain scissions and the zero-span breaking
108 strength was linear (Bégin and Kaminska 2002). Nevertheless, these studies focused on paper that underwent
109 hydrolytic degradation, without considering the possible effects of oxidation, and only a few instances report on
110 the latter (Arney and Jacobs 1980; Whitmore and Bogaard 1995).

111 In this study, the impact of the two reactions, *i.e.*, hydrolysis and oxidation, will be considered. Because these
112 reactions are slow under natural ageing conditions, artificial ageing of paper can be used to obtain degraded states

113 (Bégin and Kaminska 2002; Strlič and Kolar 2005; Jeong and Potthast 2021). Although it does not exactly replicate
114 natural ageing, this method remains valid to degrade paper since cellulose chain scissions are promoted in all cases.
115 The aim of the study is to determine the impact of different exposure conditions on the mechanical behaviour of
116 paper, and more specifically on the fibre strength, the fibre-fibre bonds resistance, and the microstructure of paper.
117 Due to the large number of structural parameters that can be involved in the embrittlement process, this multi-
118 scale approach is applied to two papers with different microstructures. The first part focuses on the evolution of
119 macroscopic mechanical properties of paper under artificial ageing conditions that favour either hydrolysis or
120 oxidation reactions. Secondly, this work intends to decouple the effects on the fibres and on the fibre-fibre bonds
121 specifically. A third part is dedicated to the evolution of the fibre resistance and the fibre-fibre bonds at the
122 microscopic scale, allowing to relate chemical changes to macroscopic mechanical behaviour.

123 **2 Experimental**

124 **2.1 Materials**

125 Two different papers were used for this study. One is a commercially available paper from Canson®, grade
126 *Barrière*, referred herein as paper A. It meets the standard for paper permanence ISO 9706. It is made from
127 bleached kraft pulp with a mix of 50 % of long fibres (softwood) and 50 % of short fibres (hardwood), and was
128 refined, according to the supplier. It contains about 3 % wt. of alkaline mineral particles (CaCO_3) to prevent the
129 acidification. Other components, such as alkyl ketene dimer (AKD) sizing and kaolin are present in minute
130 quantities. This paper was chosen because of its archival quality and essential durability for long-term preservation.
131 The second paper is a filter paper Whatman n°40 made from acid-washed cotton linters (ashless grade), referred
132 hereafter as paper B. It therefore contains only cellulose and has no additives. As opposed to paper A, it is acidic
133 and thus prone to faster degradation. It was chosen as a model since widely studied in the paper degradation
134 literature.

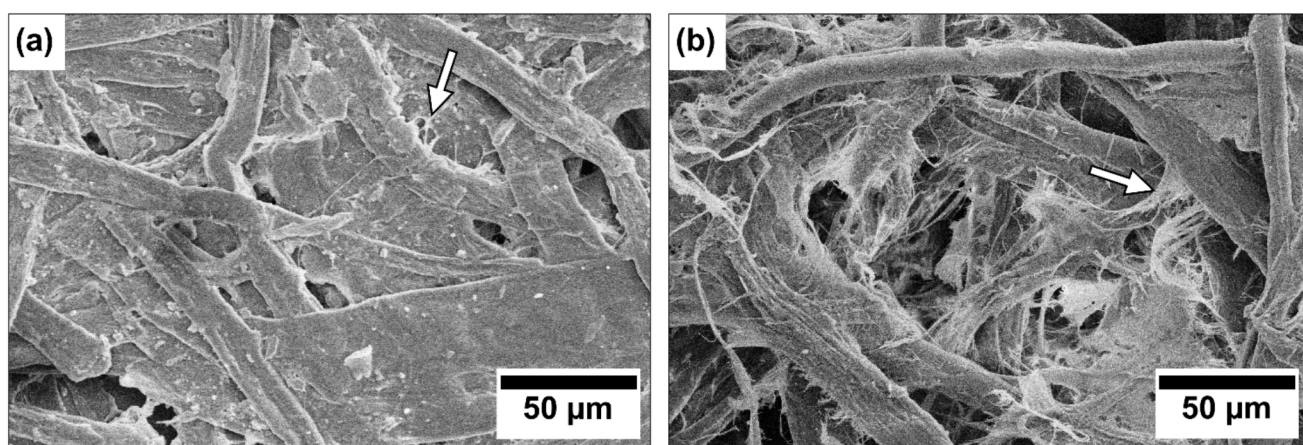
135 The main characteristics of papers A and B were measured, and their microstructures were observed, as
136 summarised in **Table 1**. The methods used are defined hereafter, e.g., size and mass measurements to calculate
137 thickness, grammage and density, MorFi analysis for fibre lengths, thermogravimetric analysis (TGA) for ash
138 content and size-exclusion chromatography (SEC) for DP. There are major differences between the two papers,
139 especially in terms of grammage and fibres length. In particular, paper A exhibits a significant difference between
140 the mean length and the length-weighted length, indicating a wider length distribution than in paper B. The long
141 fibres being responsible for the mechanical resistance, this could give paper A better strength, accordingly to the

142 fact that it should meet the mechanical criteria of ISO 9706 standard. **Fig. 1** shows the microstructure of the surface
 143 of both papers. Paper B exhibits more fibrillation than paper A, indicating more mechanical treatment like refining
 144 during papermaking process. Paper A has also flatter fibres, in coherence with his higher density.

145 **Table 1:** Main characteristics of papers A and B. Thickness and grammage were measured using a micrometric
 146 gauge and a precision weighing scale, fibre length by MorFi analysis, ash content by thermogravimetric analysis
 147 (TGA), number-average degree of polymerisation (DP_n) of cellulose by size-exclusion chromatography (SEC),
 148 and other characteristics by microscopic observations.

Characteristics	Paper A	Paper B
Thickness (μm)	100 ± 4	210 ± 3
Grammage ($\text{g}\cdot\text{m}^{-2}$)	80 ± 4	95 ± 5
Density	0.80 ± 0.04	0.45 ± 0.02
Fibres	softwood/hardwood	cotton linters
Fibres length (μm)	508 ± 5	445 ± 5
Length-weighted fibres length (μm)	870 ± 10	750 ± 10
Ash content (%)	16.4 ± 0.6	0.4 ± 0.6
DP_n of cellulose	1870 ± 30	360 ± 10

149



150

151 **Fig. 1:** Microstructure of papers A (a) and B (b) (SEM). The arrows indicate fibrillation between fibres.

152 2.2 Accelerated ageing

153 Different degradation states of the paper were achieved through exposures to artificial ageing conditions. The
 154 papers were exposed at 90 °C in closed glass tubes under different atmospheres (humid or dry, air or nitrogen) and

155 for different durations (e.g. 2, 4, 10, 25 and 50 weeks). Before exposure, the papers were prepared as follows: the
156 sheets were cut in strips of 15 mm × 120 mm in the two directions of the sheet to enable mechanical testing in the
157 main direction of the fibres (machine direction, referred hereafter as longitudinal direction) and in the
158 perpendicular direction (cross direction, referred hereafter as transverse direction). About 20 to 30 strips
159 (equivalent to 4 g of dry paper) were introduced in 15 cL Wheaton® glass tubes.

160 Two tubes per ageing duration were preconditioned under each specific atmosphere:

- 161 • 50 % RH in a climate room at 23 °C for 48 h (*humid air*)
- 162 • 0 ppm oxygen and 50 % RH in a glovebox at 23 °C for 48 h (*humid nitrogen*)
- 163 • circa 0 % RH in an oven at 105 °C for 2 h (*dry air*)
- 164 • circa 0 ppm oxygen and 0 % RH in a glovebox at 23 °C for 48 h (*dry nitrogen*)

165 The tubes were closed with a polypropylene screw cap and a PTFE septum insert (Duran Groups®, max. 140 °C).
166 A three-layered film (PET, aluminium, polyethylene) was added on the tubes opening to improve tightness. They
167 were then aged at 90 °C in the following conditions:

- 168 • 50 % RH in an environmental chamber (*humid air and humid nitrogen*)
- 169 • circa 0 % RH in an oven (*dry air and dry nitrogen*)

170 **2.3 Chemical analysis**

171 The degree of polymerisation (DP) of cellulose was measured by size-exclusion chromatography (isocratic HPLC
172 pump Waters® 515 at 0.4 mL·min⁻¹ and 100 µL injection volume, autosampler Dionex® UliMate 3000, 4 columns
173 Agilent® PLGel miniMIX A (20 µm and 4.6 mm × 250 mm) thermostated at 60 °C, MALS detector Wyatt
174 Technologies® Dawn EOS at 60 °C, differential reflective index detector Waters® 2414 at 55 °C). Samples about
175 10.4 mg of paper were prepared and analysed three times according to Dupont (Dupont 2003). Astra® 5.3.4.14,
176 Wyatts Technologies® was used for the data acquisition and analysis.

177 The ash content in the papers was measured by thermogravimetric analysis (TGA), with a TA Instrument® TGA
178 Q50 apparatus controlled via QSeries™ software at a scanning speed of 10 °C per minute until 800 °C, under
179 nitrogen at a flow rate of 90 mL·min⁻¹. The reported ash content corresponds to the relative mass remaining at
180 800 °C.

181 2.4 Mechanical tests

182 Mechanical tests were carried out in a climate room at 23 °C and 50 % RH. The unaged and aged paper strips
183 (15 mm × 120 mm) were conditioned for at least 48 hours in the climate room before the tests. Paper is an
184 anisotropic material due to its fabrication process, leading to a mean orientation of the fibres along the machine
185 direction. These tests were therefore performed in the two main directions of the sheet, *i.e.* the main direction of
186 the fibres (machine direction), and the perpendicular axis (cross direction), referred herein as longitudinal and
187 transverse directions, respectively.

188 The mechanical tests were adapted from TAPPI standards T 494 om-01 for tensile properties, T 511 om-02 for
189 folding endurance and T 231 cm-96 for zero-span breaking strength. For tensile test, a DY20 Adamel Lhomargy
190 dynamometer coupled with an MTS Systems® TestWorks software was used with the following setting: 5 cm of
191 span between the jaws, speed of 1 mm·min⁻¹, fracture detection at 50 % of the maximal stress. Folding endurance
192 tests were realised on a Tinius Olsen® MIT folding tester at a speed of 200 folds per minute and a bending angle
193 of 270°. The initial applied stress was equivalent to 500 g instead of 1 kg because of the low resistance of the most
194 degraded papers. For zero-span tensile tests, a Pulmac® Z-span tester was used. The clamping pressure used was
195 410 kPa (60 psi), as it was the maximum stable pressure authorised by the installation and is sufficient to prevent
196 slippage (Batchelor et al. 2006).

197 Each result is the average of several repeat measurements using strips from the two ageing tubes of each exposure
198 condition. For tensile tests, 6 strips were tested for paper A, and 4 strips for paper B, in the two directions. The
199 tests for which strips broke within 1 cm distance to the jaws were considered as invalid. For zero-span tensile and
200 folding endurance tests, at least 10 strips were used for each paper and exposure conditions.

201 All the DP_n and mechanical testing data used to draw the following graphs are available in a Supplementary
202 Information file (**Table S1**).

203 2.5 Observations on the microstructure

204 The microstructure of the paper surface was observed by scanning electron microscopy (SEM), using a Hitachi®
205 4800 microscope. Prior to the observation, the samples were metallised through a gold deposition process (2
206 minutes at 1.2 kV and 5 mA). The observations were conducted at an acceleration of 5 to 10 kV and 10 mA, and
207 detection was performed using two secondary electron (SE) detectors positioned at high and low angles.

208 Fracture surface of paper strips were observed through a Zeiss® SteREO Discovery V.20 binocular lens with a
209 $\times 2$ objective, coupled with Archimed® software. Three images were recorded for each strip at the failure zone,
210 resulting in 18 images for each ageing condition for paper A and 12 images for paper B. These images were treated
211 with ImageJ® software to measure the mean extracted fibre lengths at failure surface.

212 Microstructure characteristics of the fibres were obtained with a MorFi LB01 instrument at Pagora, Grenoble INP,
213 France. MorFi analysis consists in gathering images of fibres in suspension. Paper is first defibrated in water; the
214 obtained pulp is continuously pumped into the system and monitored with a speed camera. Several dozens of fibres
215 are captured for each image, and multiple images can be recorded within a few minutes. This technique is both
216 fast and statistical.

217 The samples for MorFi analysis were prepared as follows: about 2 g of paper are weighted and placed in hot water
218 (around 65 °C) during a few hours. The volume of water is adjusted to a concentration of 1 g·L⁻¹. The rehydrated
219 paper is then defibred in a blunt blades pulper for 5 minutes at 50 Hz, adding 5 minutes if the defibration was not
220 complete. Each pulp suspension is sampled in three replicas of 300 mg and ran through the MorFi machine; a
221 fourth sample is measured in case the repeatability criteria are not met (standard deviation below 20 µm on length
222 and 0.2 µm on diameter). MorFi software is set to stop the analysis after 50,000 elements detected as fibres (length
223 between 0.1 and 10 mm and diameter between 5 and 75 µm) are measured.

224 **3 Results and discussion**

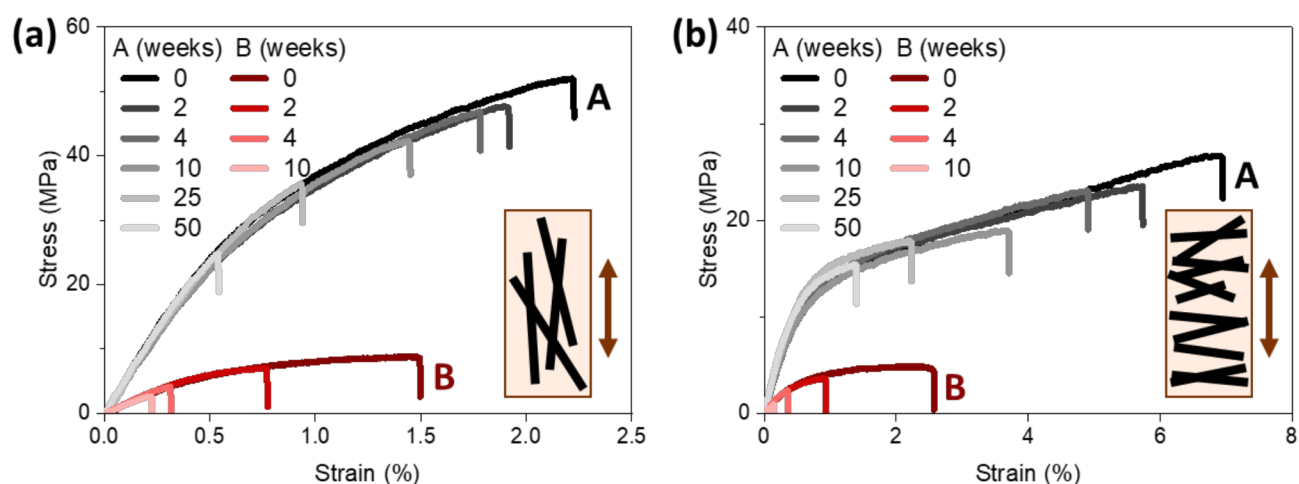
225 **3.1 Macroscopic scale: mechanical behaviour**

226 To follow macroscopic embrittlement, the behaviour of the two papers aged under different conditions and
227 subjected to tensile test and folding endurance test is examined to evaluate the consequences of hydrolysis and
228 oxidation reactions.

229 **3.1.1 Embrittlement process**

230 The stress-strain curves from tensile tests in the two main orientations of the fibres are presented in **Fig. 2** for the
231 two papers aged under humid air conditions. The shape of the curves is characteristic of the elastoplastic behaviour
232 of paper (Hill et al. 1995; Fernández-Diego et al. 2021). First, the mechanical properties at the unaged stage are
233 presented in order to exhibit the structure-properties relationship for the two papers (**Table 2**). Stress at break and
234 elastic modulus are normalised by the density of the papers. Brittleness index is defined by Zou as the ratio of
235 elastic strain energy to the total tensile energy absorption (TEA) at the time of failure (Zou et al. 1994).

236



237

238 **Fig. 2:** Stress-strain curves for papers A and B in the longitudinal direction of the fibres (a) and in the transverse
 239 direction (b), at unaged state and after ageing for 2 to 50 weeks under humid air conditions.

240 **Table 2:** Tensile properties of unaged papers A and B in longitudinal and transverse directions: stress at break
 241 and elastic modulus are normalised, *i.e.* divided by the density of paper. Brittleness index is the ratio of elastic
 242 strain energy to the total tensile energy absorption at the time of failure.

	Paper A		Paper B	
	Longitudinal direction	Transverse direction	Longitudinal direction	Transverse direction
Normalised stress at break (MPa)	58.5 ± 1.9	29.9 ± 1.6	19.4 ± 0.3	10.4 ± 0.7
Strain at break (%)	2.2 ± 0.2	6.4 ± 0.7	1.5 ± 0.1	2.3 ± 0.2
Normalised elastic modulus (GPa)	5.9 ± 0.2	2.9 ± 0.3	3.0 ± 0.1	1.8 ± 0.1
Brittleness index (%)	33.8 ± 3.4	10.7 ± 0.8	42.1 ± 3.6	25.6 ± 4.4

243

244 Large discrepancies between paper A and paper B were found (**Table 2**): at unaged state, paper B has smaller
 245 normalised stress at break, normalised elastic modulus, and strain at break than paper A in both directions. Its
 246 brittleness index is higher, corresponding to a more fragile behaviour. To explain these observations, the initial
 247 characteristics of the papers were measured (**Table 1**). Even if paper B exhibits higher degree of refining (**Fig. 1**),
 248 it has a lower density, slightly shorter fibres, and a considerably lower DP_n of cellulose, all of which suggests
 249 weaker network and weaker fibre resistance (Bronkhorst 2003; Picu 2021). Moreover, the papermaking process

250 of paper A includes the addition of strengthening agents such as the sizing. Its higher strength is coherent with its
251 use as a printing paper, compared to paper B, which is designed for filtering and hence has no additives. Paper A
252 is also more rigid than paper B as indicated by the much higher elastic modulus. This can be explained by its higher
253 density that increases the probability of fibre-fibre bonding, which is responsible for more rigid networks.

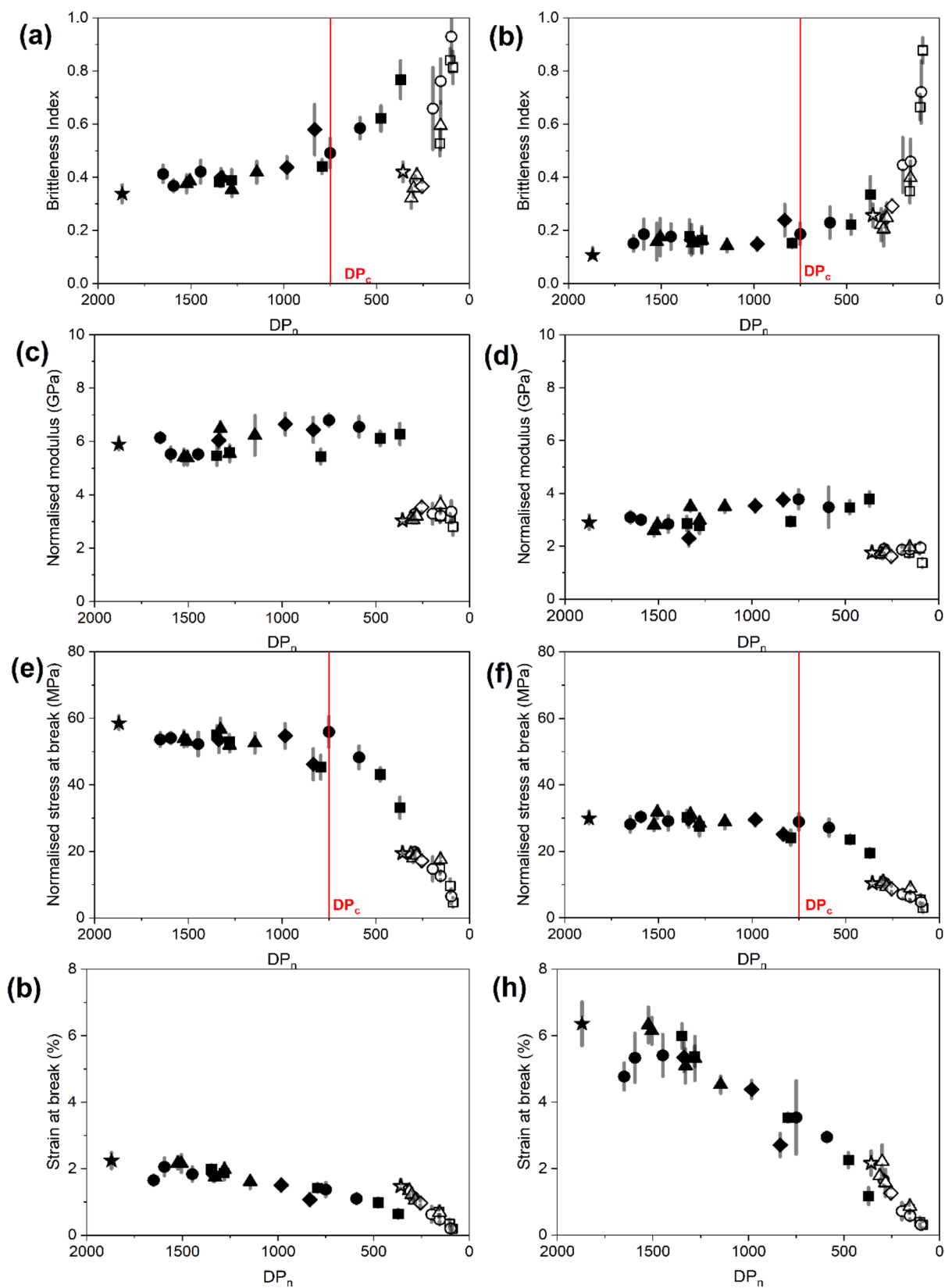
254 **Table 2** also shows the anisotropy of the papers: as expected, the transverse direction exhibited smaller normalised
255 elastic modulus and brittleness index, leading to larger strain at break for both papers (Cox 1952; Leheny et al.
256 2021). The anisotropy can be quantified through the ratio of elastic modulus in longitudinal to transverse direction.
257 This ratio is 2.0 in the case of paper A, and 1.7 for paper B. The larger anisotropy of paper A can be explained by
258 a different fabrication process. Moreover, in the inelastic zone of the strain-stress curve, the slope is smaller in the
259 transverse direction. The difference in the inelastic behaviour is also linked to the fibre orientation. This could be
260 explained by rearrangement processes: in the transverse direction, the fibres have more degree of freedom to align
261 with the tensile axis than in longitudinal direction. This leads to two to three times higher strain at break.

262 As shown on **Fig. 2**, the artificial ageing leads to earlier failure: the strength and the strain at break decrease, but
263 the elastic modulus remains stable, as confirmed by the literature (Kurei et al. 2022). The embrittlement of paper
264 B occurs for shorter exposure times than that of paper A. After a 10-week ageing, it reaches a strength for which
265 paper is hardly manipulable. The evolution of the mechanical properties with ageing is presented below.

266 **3.1.2 Correlation between mechanical properties and chemical degradation**

267 The detailed evolution of tensile test parameters is illustrated in **Fig. 3** for both papers aged under the different
268 exposure conditions, and in the two main directions. The chemical degradation state is expressed in terms of
269 number-average degree of polymerisation (DP_n), value used to calculate the length of cellulose chain, knowing
270 that both ageing mechanisms, hydrolysis and oxidation, lead to chain scissions. DP_n data for paper A and B aged
271 under humid air, humid nitrogen, and dry air up to 10 weeks have been presented from a kinetic point of view in
272 recent work (Vibert et al. 2023). It showed in particular that the presence of oxygen enhanced the degradation of
273 both papers, and that the degradation of paper B was faster than that of paper A whatever the ageing condition.

274



275

276 **Fig. 3:** Evolution of mechanical properties with the decrease of degree of polymerisation, as measured by tensile
 277 test for the two papers in the longitudinal direction (a, c, e, f) and in the transverse direction (b, d, f, h) upon all
 278 exposure conditions for different durations between 0 and 50 weeks at 90 °C (initial values ★, humid air ■,

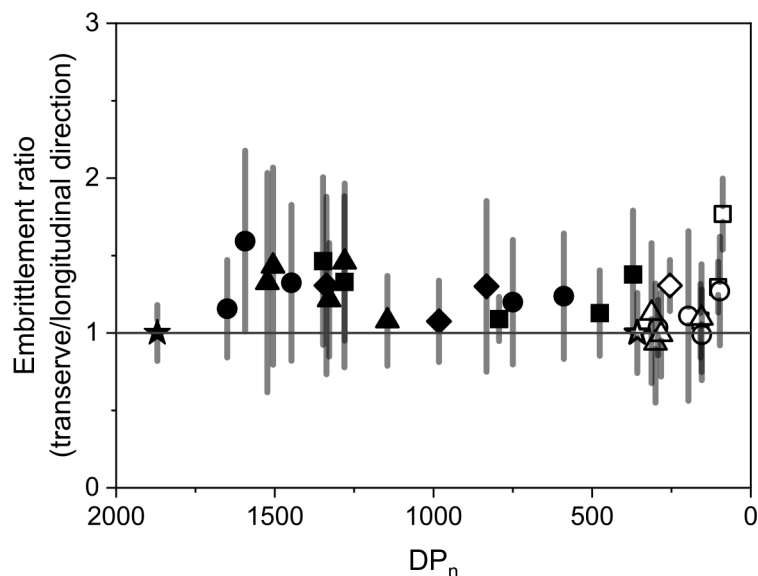
279 humid nitrogen ●, dry air ▲, dry nitrogen ◆, full symbols for paper A and empty symbols for paper B). The
280 vertical red line indicates the value of critical DP_n .

281 **Fig. 3** shows that the evolution of the mechanical parameters of the two papers followed the same trend
282 independently of the orientation of the fibres and the exposure conditions. Papers become increasingly more brittle
283 as shown by the increase of the brittleness index, and a concomitant decrease of the stress and the strain at break,
284 while the elastic modulus remains constant.

285 Interestingly, the data points for a given paper and direction align on a unique curve as a function of DP_n . In other
286 words, the embrittlement process is independent of the exposure conditions. This confirms the zero-span tensile
287 strength data of Zou for acidic paper (Zou et al. 1994). However, to our knowledge in the case of permanent paper,
288 which is reported to be more prone to oxidation (Kolar 1997), this result had not been reported before. In particular,
289 it demonstrates that, even when oxidation plays a role in the chemical degradation (Vibert *et al.*, 2023), this does
290 not lead to a different mechanical behaviour of the paper. The influence of oxidation on the embrittlement process
291 could have been expected as certain types of oxidation mechanisms could impact hydrogen bonding, as for
292 example the oxidation of hydroxyl groups into carbonyl groups along the glucose ring (Kolar 1997). However,
293 this has been shown to be negligible (Ahn et al. 2012). This would have reduced the number of donors of hydrogen-
294 bonds, which are responsible for bonding in the fibres, and at fibre-fibre bonds. In this study, such behaviour was
295 not observed, thus oxidative exposure conditions do not lead to fibre-fibre bonds degradation.

296 **Fig. 3** also exhibits the existence of a critical DP for paper A, under which the decrease of normalised stress at
297 break accelerates. According to the brittleness index and to the normalized stress at break as a function of DP_n , the
298 critical DP_n associated to the beginning of the embrittlement process lies between 500 and 1000. The existence of
299 a critical DP (DP_c) was notably shown in the literature in relation with the zero-span tensile tests (Zou et al. 1993);
300 this point will be discussed below. It was not observed for paper B, for which the initial DP_n value is already below
301 500 due to the acidic manufacturing process, which decreases the DP.

302 A slight decrease in the slopes of the curves on **Fig. 3** prior to reaching the DP_c , after which a more significant
303 decrease of the mechanical property occurs, was observed for both stress at break and brittleness index of paper
304 A. Conversely, the strain at break exhibited an almost linear decrease, and again no evolution was observed for
305 the elastic modulus. This latter observation is consistent with the literature (Zou et al. 1994; Kurei et al. 2022).
306 Since the elastic modulus is partly related to the elasticity of fibre-fibre bonds, the authors suggested that its
307 constancy may be explained by the absence of degradation of the bonds.



308

309 **Fig. 4:** Embrittlement ratio (transverse vs longitudinal directions variation in the brittleness index) as a function
 310 of DP_n (initial values ★, humid air ■, humid nitrogen ●, dry air ▲, dry nitrogen ◆, full symbols for paper A and
 311 empty symbols for paper B).

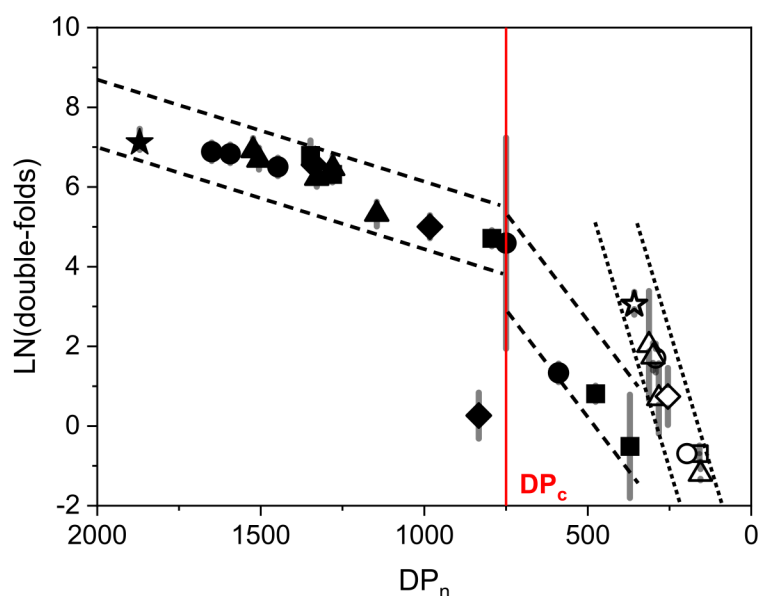
312 To illustrate the relative variation of the mechanical properties as a function of the direction of the stress, and
 313 hence the influence of the orientation of the fibres in the embrittlement process, an embrittlement ratio is shown
 314 in **Fig. 4**. This embrittlement ratio (ER) was calculated as the embrittlement in the transverse direction (T) over
 315 the embrittlement in the longitudinal direction (L) of the fibres, the embrittlement being the variation of brittleness
 316 index with ageing, *i.e.* the brittleness index at a given degraded state $BI(t)$ over the initial state $BI(0)$:

$$317 \quad ER(t) = (BI_T(t) / BI_T(0)) / (BI_L(t) / BI_L(0)) \quad (1)$$

318 ER expresses if one direction exhibits faster embrittlement than the other. This ratio remained above 1 for both
 319 papers, showing that the transverse direction underwent faster embrittlement than the longitudinal direction
 320 ($BI_T(t) / BI_T(0) > BI_L(t) / BI_L(0)$). In the longitudinal direction, the fibres are aligned with the direction of the
 321 principal stress, and the fibre-fibre bonds are under little stress. On the contrary, in the transverse direction, the
 322 fibres are oriented perpendicular to the load direction, which leads to the fibre-fibre bonds being sheared.
 323 Moreover, in the latter configuration, the reorientation of the fibres during the mechanical loading also leads to
 324 bending the fibres (Deshpande et al. 2001; Syerko et al. 2012). It can be concluded that during ageing, either the
 325 fibre-fibre bonds are damaged, or the fibres are less resistant to bending. Since the constancy of elastic modulus
 326 gave clues for bonds stability, the second hypothesis applies.

327 3.1.3 Fatigue properties: folding endurance

328 The papers were also tested for mechanical fatigue in the longitudinal direction. Folding endurance is a localised
 329 bending fatigue test. The results for all the ageing conditions are shown in **Fig. 5**. Again, the decrease in the folding
 330 endurance does not depend on the ageing condition. It appears to be linear with the DP_n for paper B, as well as for
 331 paper A up to approaching degradation levels corresponding to the DP_c . This critical DP_n , identified by the slope
 332 break, is again around 750. The slope is also stiffer than for tensile properties as a function of DP_n , similarly to
 333 tensile fatigue tests that highlight the effect of chemical degradation (Yue et al. 2019).



334
 335 **Fig. 5:** Evolution of the folding resistance in longitudinal direction with the degradation, as expressed as the
 336 logarithm of the mean number of double-folds at break (initial values ★, humid air ■, humid nitrogen ●, dry air
 337 ▲, dry nitrogen ◆, full symbols for paper A and empty symbols for paper B). The vertical red line indicates the
 338 value of critical DP_n .

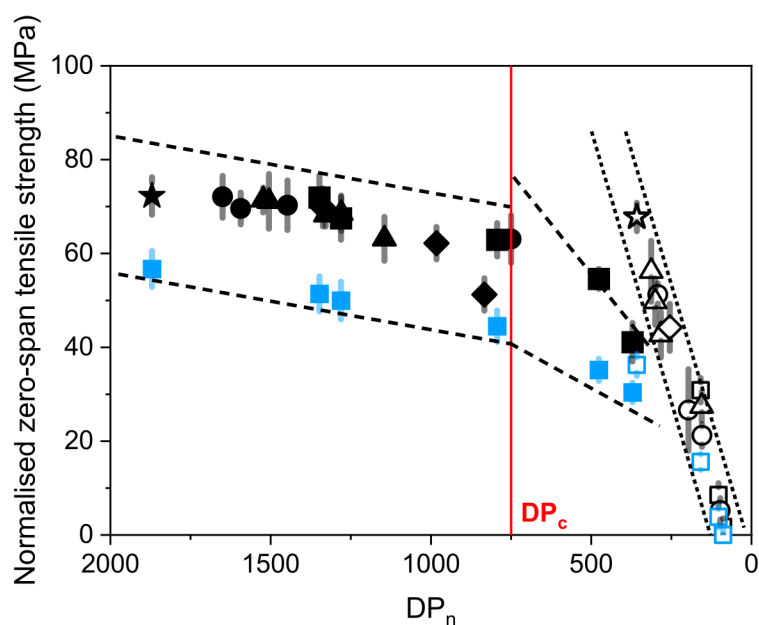
339 It is interesting to note that the critical DP_n for folding endurance to start showing a faster decay is the same as for
 340 stress at break. This suggests that the damage mechanisms in the folding and tensile tests are bound to similar
 341 chemical degradation mechanisms. For both tests, stress is applied on both fibres and fibre-fibre bonds. However,
 342 during folding, bending applies more on the fibres than on the bonds because the strain is localised on a precise
 343 section of the paper. During tensile tests, the stress is distributed in all the sample, and applies to both fibres and
 344 fibre-fibre bonds. Therefore, the stress applied on the fibre-fibre bonds is different for tensile and folding test. This
 345 would suggest that the DP_c mechanism relates more specifically to the fibre and not to the fibre-fibre bonds.

346 3.2 Mesoscopic scale: decoupling the mechanical behaviour of fibre and fibre-fibre bonds

347 The decrease in paper strength relates to the location of the embrittlement mechanism, predominantly at fibre-
 348 fibre bonds or within the fibres. To decouple the effects, the zero-span tensile test was used as a fibre-specific
 349 test, providing information on the intrinsic degradation of the fibres.

350 3.2.1 Zero-span tensile tests

351 **Fig. 6** shows the normalised zero-span tensile strength of the two papers aged in the different conditions.
 352 Confirming the earlier results on the tensile properties, for a given paper and in a specific direction all the data
 353 points aligned on the same curve, showing no individual effect of the oxidation or the hydrolysis on the mechanical
 354 degradation of fibres. As with the other mechanical tests, differences between the papers and dependency on the
 355 fibre's direction are visible.



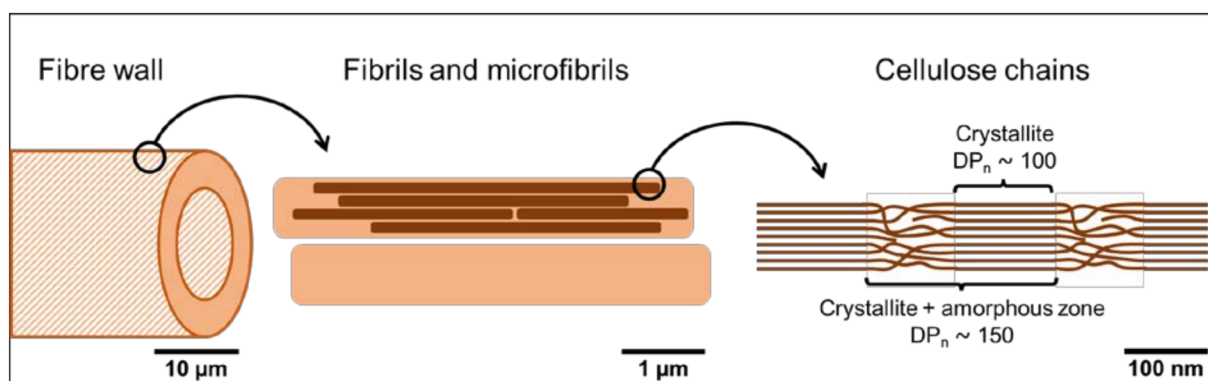
356 **Fig. 6:** Zero-span tensile strength normalised by the density of paper in the two principal directions vs DP_n
 357 (initial values ★, humid air ■, humid nitrogen ●, dry air ▲, dry nitrogen ◆, full symbols for paper A and empty
 358 symbols for paper B, black for longitudinal direction and light blue for transverse direction). The vertical red line
 359 indicates the value of critical DP_n .

361 The value of zero-span tensile strength of the unaged samples in the transverse direction is higher than that for the
 362 stress at break in the normal tensile test, being 72.3 and 58.5 MPa for paper A and 67.8 and 19.4 MPa for paper B,
 363 respectively. This can be due to the fact that zero-span tensile test is localised (Wathén et al. 2005), *i.e.* the stress

364 is applied on both sides of a section of the sheet. The resulting strength is the average strength of a randomly
365 selected section in the paper sheet, whereas during tensile test, the paper sheet breaks at the weakest section.

366 As for tensile test, in the transverse direction, the zero-span resistance is lower than in the longitudinal direction
367 at all equivalent degradation states and conditions. By volume conservation, the surface of fibres in a longitudinal
368 as in a transverse section is the same. However, due to the alignment of cellulose chains in the crystallites almost
369 parallelly with the direction of the fibre (Young and Rowell 1986), fibres should be more resistant under
370 longitudinal tensile, where cellulose chains are stressed, than under transverse tensile, where hydrogen bonds
371 between cellulose chains are. The higher zero-span tensile strength in the longitudinal direction of the paper can
372 simply be explained by the much larger number of fibres passing through a given section if the latter is
373 perpendicular to the direction of fibres than if it is parallel to the direction of fibres.

374 As observed for other tests, paper A exhibited a shallow decrease in the high DP_n ranges, and a steeper decrease
375 after the $DP_c = 750$. This would indicate that the embrittlement mechanism is more related to the fibre than to the
376 fibre-fibre bond. Again, no slope break, and hence no critical DP_n , was observed for paper B for which the initial
377 DP_n is already below 750. This is consistent with the literature, where a critical DP in zero-span tensile test was
378 observed between 500 and 1000 (Zou et al. 1994; Tétreault et al. 2019). However, to our knowledge, no
379 explanation for the existence of a critical value has been proposed. Such degree of polymerisation threshold has
380 been observed for conventional semi-crystalline polymers (Fayolle et al. 2008). It is associated with the critical
381 molar mass to ensure a minimum thickness of amorphous phase, which is responsible for plastic deformation
382 mechanisms. However, the specific fibrillar and microfibrillar structure of cellulose adds a level of complexity.
383 Given the fibre morphology, schematised in **Fig. 7**, a DP of 750 corresponds to 4 or 5 units of crystalline plus
384 amorphous zones, considering that the crystallinity of paper is 70 % and that the LODP of 100 corresponds to the
385 average length of a crystallite (Young and Rowell 1986). It also corresponds to an average of 1.5 scissions per
386 cellulose chain for paper A. This might be the average degradation level under which transfer of applied stress
387 along the fibres and through fibre-fibre bonds becomes less efficient.



388

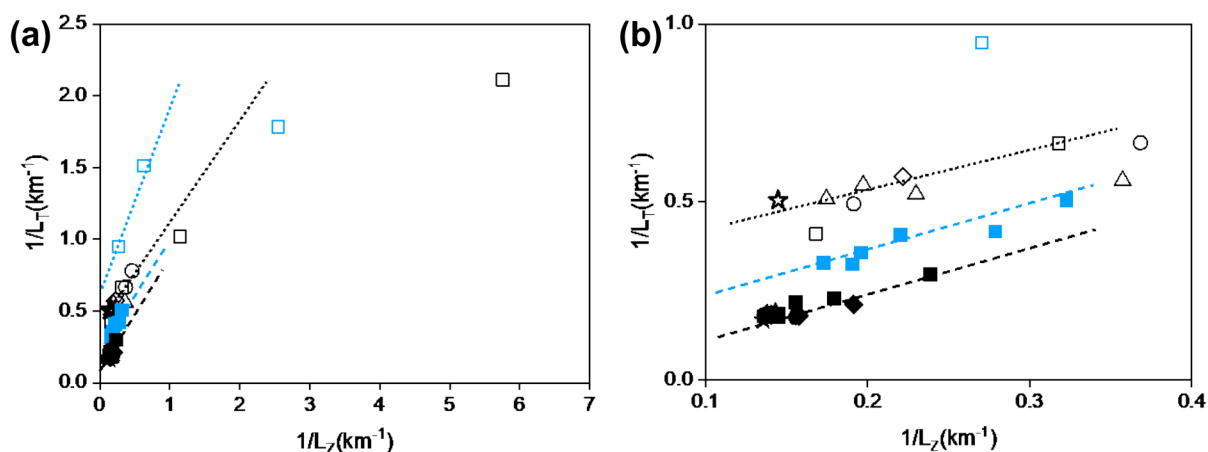
389 **Fig. 7.** Schematic representation of the microstructure of a cellulose fibre at the scale of the fibre, the fibrils, and
 390 the cellulose chains according to (Kortschot 1997) and (Young and Rowell 1986).

391 3.2.2 Page equation

392 The results of the zero-span tensile tests and of the tensile strength tests showed the evolution of the paper strength.
 393 The comparison between these values can be used to assess the contribution of fibre-fibre bonds to the paper
 394 strength, and how it evolves with ageing. In this regard, the semi-empirical Page equation relates the two tests as
 395 follows (Page 1969):

$$396 \quad 1/L_T = 9/8 * 1/L_Z + 12g/bL\alpha \quad (2)$$

397 with L_T and L_Z being respectively the breaking length in tensile and in zero-span tensile test (in km), *i.e.*, the
 398 equivalent length of paper for which the strip breaks under its own weight, g the standard acceleration due to
 399 gravity, b the surface shear bonding strength (in $\text{kg}\cdot\text{m}\cdot\text{s}^{-2}$), L the mean fibre length (in m), and α the contact area
 400 relative to the mass of paper (in $\text{m}^2\cdot\text{g}^{-1}$). $bL\alpha$ represents the shearing bonding of the paper. This equation expresses
 401 the fact that tensile resistance arises both from fibre resistance and fibre-fibre bonding.



402

403 **Fig. 8:** (a) Graphical representation of the Page equation for papers A and B, with L_T the tensile breaking length
 404 and L_Z the zero-span breaking length. The data points in the lower inverse length area being aggregated, (b) zoom
 405 of (a) (initial values ★, humid air ■, humid nitrogen ●, dry air ▲, dry nitrogen ◆, full symbols for paper A and
 406 empty symbols for paper B, black for longitudinal direction and light blue for transverse direction).

407 **Table 3:** Parameters of the Page equation for papers A and B: $1/L_T = a/L_Z + 12g/bLa$, with the correlation
 408 coefficient r^2 for papers aged under humid air.

Paper	Direction	Exposure condition	a	r^2	bLa ($km^2 \cdot s^{-2}$)
A	Longitudinal	humid air	1.18	0.97	6.8
		all conditions	1.08	0.85	4.3
	Transverse	humid air	1.11	0.91	0.9
B	Longitudinal	humid air *	1.20	0.77	0.4
		all conditions *	0.80	0.78	0.3
	Transverse	humid air *	1.57	/	0.2

409 * For paper B, the data for 4 and 10 weeks under humid air conditions were not included because of excessive damage.

410 To assess the validity of Page model in the case of artificial ageing of paper due to hydrolysis and oxidation, tensile
 411 and zero-span breaking lengths were plotted in **Fig. 8**. The curve was not linear for high values of $1/L_T$. However,
 412 most data set points of a same paper and orientation were aligned. The four data points that exhibited non-linear
 413 behaviour correspond to the highest degradation states of paper B, *i.e.* aged for 4 and 10 weeks in humid air
 414 conditions. In terms of DP , these samples have reached the levelling-off degree of polymerisation (LODP), e.g.
 415 the DP for which where the kinetics of cellulose hydrolysis slows down tremendously (Battista et al. 1956;
 416 Stephens et al. 2008). At this advanced stage of degradation, Page model is no longer valid. However, it is
 417 interesting to note that Page equation is valid before reaching the LODP, even for DP values lower than the DP_c
 418 of 750 defined previously.

419 The parameters in the Page equation were assessed in the linear regime of the slopes. **Table 3** presents the results
 420 of the linear regressions. The slope, named a , between zero-span and tensile breaking lengths is found to be close
 421 to 9/8 for both papers. In Page's equation, this value of 9/8 accounts for the Poisson ratio of the paper being of 1/3.
 422 As a comparison, Zou found a slope around 1.25 for the same paper as paper B aged in humid air, which is slightly
 423 above that of Page (Zou et al. 1994). It is not surprising that the slopes that were found here are not exactly those

424 of Page or Zou, according to the fact that the Poisson ratio of the paper depends on the fibre orientation (Cox
425 1952), and may depend on the nature and processing of the fibres.

426 Furthermore, **Table 3** shows that the linear regression is less accurate when all the data points are included. Since
427 the ageing conditions were found to have no differentiated impact on the mechanical embrittlement, this
428 observation can be explained by the fact that, except for the humid air condition, the embrittlement level is low,
429 and the data points are therefore clustered.

430 Page equation also gives an estimate of the shear bonding bLa . This parameter is reported in **Table 3**. It is higher
431 for paper A than for paper B. This can be explained by a difference in bonding strength, in fibre length, or in
432 contact area. As shown in **Table 1**, the fibres in paper A are in average longer by 15 % than in paper B and the
433 density of paper A about two times higher. Assuming that density is almost linear with contact area (Sampson
434 2003), the a parameter of paper A is also twice that of paper B. Taking into account these ratios, the surface shear
435 bond b in paper A would be around 8 times higher than that in paper B.

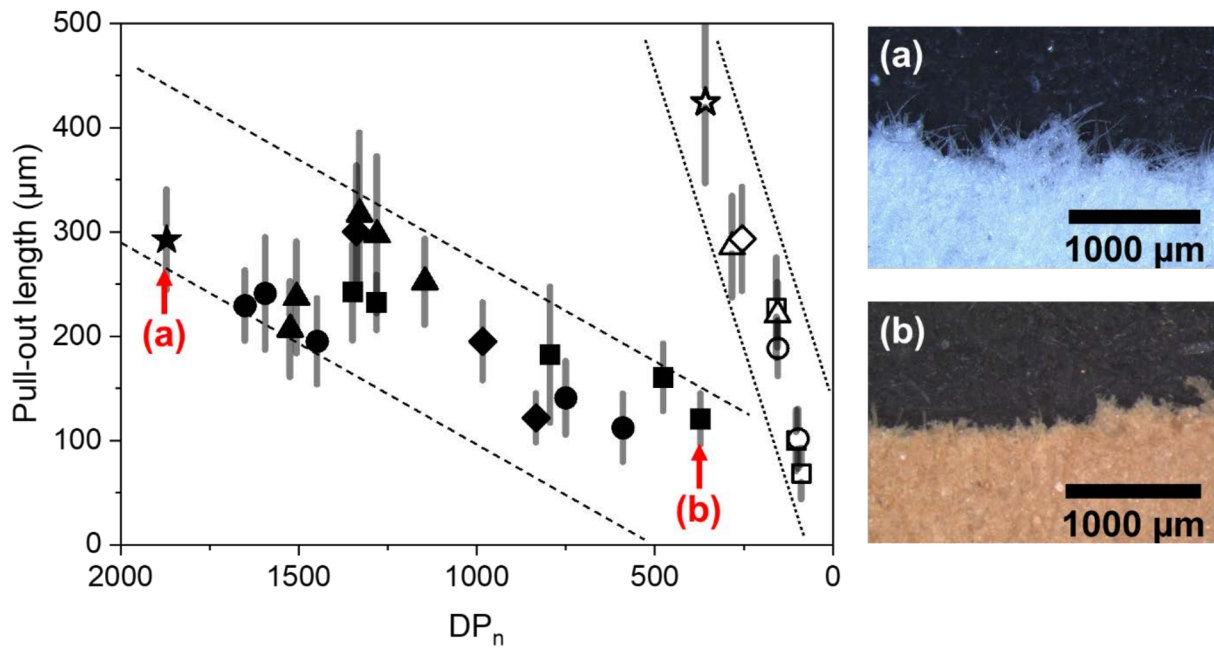
436 **Table 3** shows an unexpected difference between the longitudinal and transverse directions, even more pronounced
437 for paper A. Indeed, according to the definition provided by Page, none of the b , L and a parameters are defined
438 as dependent on the direction of the fibres. However, it can be presumed that b is in fact dependent on the
439 orientation, as it can account for the projection of bonding shear along the considered axis. This explanation is
440 consistent with the fact that fibre-fibre bonds are not submitted to the same stress depending on the orientation.

441 **3.3 Microscopic scale: Morphology of the fibres**

442 The microstructure of paper was evaluated using two different and complementary techniques: localised
443 observations of the fracture surfaces to obtain *in situ* information, and MorFi analysis that enables a statistical
444 evaluation of the morphology of fibres.

445 **3.3.1 Fracture surfaces**

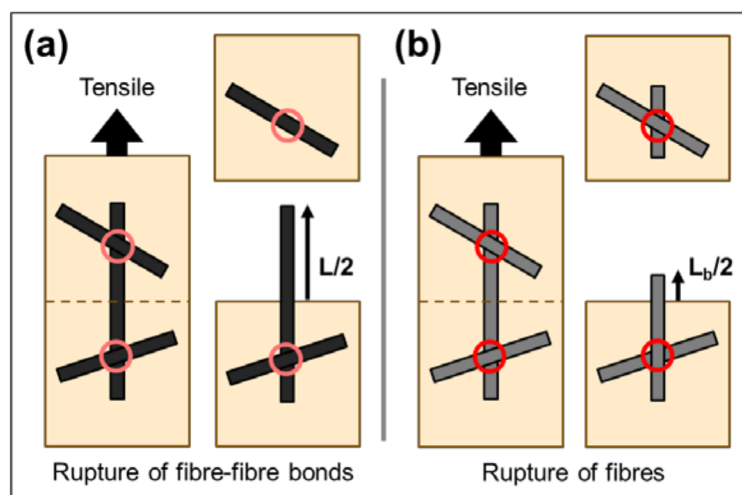
446 To evaluate the impact of ageing on the rupture mechanism of the papers, the fracture surfaces after tensile tests
447 were observed and the length of pulled-out fibres was measured. The results, reported in **Fig. 9**, show that the pull-
448 out length decreased for both papers as function of DP_n . Furthermore, this evolution seems almost linear with DP ,
449 with a steeper slope for paper B than for paper A.



450

451 **Fig. 9:** Evolution of the mean length of the pulled-out fibres in the fracture zone for longitudinal direction tensile
 452 tests ($\Delta = 50 \mu\text{m}$) as a function of DP_n (initial values \star , humid air \blacksquare , humid nitrogen \bullet , dry air \blacktriangle , dry nitrogen
 453 \blacklozenge , full symbols for paper A, and empty symbols for paper B). Microscopy images of fracture surfaces for paper
 454 A at initial state (a) and after 50-week in humid air (b).

455 The pull-out length depends on the slippage of fibres at the fracture surface (Wathén et al. 2005). If the fracture is
 456 due to the rupture of the fibre-fibre bonds (**Fig. 10a**), the fibre at fracture surface would entirely slip out the
 457 network, and the pull-out length would be in average equal to half the fibre length (as half of the fibre would stay
 458 in each part of the broken strip, in average). On the contrary, if the fracture is due to rupture of the fibres while the
 459 fibre-fibre bonds remain constant (**Fig. 10b**), only the length equivalent between two bonds would slip, and the
 460 pull-out length would be equal to half of the average bond-to-bond length.



461

462 **Fig. 10:** Scheme of the pull-out length at fracture surface for embrittlement of either fibre-fibre bonds (red circles)
463 (a) or fibres (b), with L the fibre length and L_b the bond-to-bond length.

464 The initial pull-out length of paper A and B are about 300 μm and 550 μm , respectively. Compared to the fibre
465 length of both papers (508 and 445 μm , respectively (**Table 1**)), these values are significantly higher than expected,
466 *i.e.* 254 and 223 μm maximum, respectively. This can be explained by a measurement bias. Indeed, the longer
467 pulled-out fibres are better detected in the binocular lens images, and the smaller fibres might not be measured
468 using ImageJ® software. The measured pull-out length is therefore higher than the actual pull-out length.
469 However, since measurements and image treatments were done in the same manner for all the images, the
470 comparison upon ageing is still relevant.

471 It can also be stressed out that, at the initial stage, paper B exhibited longer extracted fibres than paper A, even if
472 its fibres are in average shorter. This can be justified by the differences in the average number of contacts and
473 fibre-fibre bonding strength. The lower density of paper B could explain less contact between the fibres, and
474 therefore longer bond-to-bond length. On the other hand, the absence of additives, such as AKD sizing or fillers,
475 induces weaker bonding between fibres. These two factors lead to longer pull-out. Moreover, the presence of fine
476 elements and strengthening additives can reinforce the bounding, and thus a lower pulled-out length. This can also
477 explain the stiffer slope (**Fig. 9**), as fibre strength becomes all the more predominant in pull-out lengths in the case
478 of paper B.

479 The general decrease of pull-out length can be interpreted as a decrease of the fibre strength. Indeed, if the fibre
480 strength remained constant, the fibre-fibre bonds should be responsible for the diminution. To achieve such
481 diminution, it would require a decrease of bond-to-bond length, *i.e.* an increase of the number of fibre-fibre bonds,
482 or an increase of bonding strength. None of these hypotheses have been reported in the literature, nor do they seem
483 consistent with chemical degradation or paper morphology. Fracture surfaces provide therefore further evidence
484 of the embrittlement being due a decrease in the fibre strength.

485 3.3.2 Fibres length and shape

486 The morphology features of fibres were measured using a MorFi analyser. This technique is based on image
487 analysis of paper pulp, *e.g.*, fibres in suspension in water. It has to be noted that the repulping process induces
488 mechanical stress on the fibres during their separation, which can lead to earlier fibre break. The length measured
489 by MorFi is therefore referred hereafter as repulped fibre length, as opposed to *in situ* fibre length. Moreover, the

490 image analysis can induce a bias since only elements with sizes included between 0.1 and 10 mm length and
 491 between 5 and 75 μm thick are considered as fibres by the software, smaller elements being considered as fines.

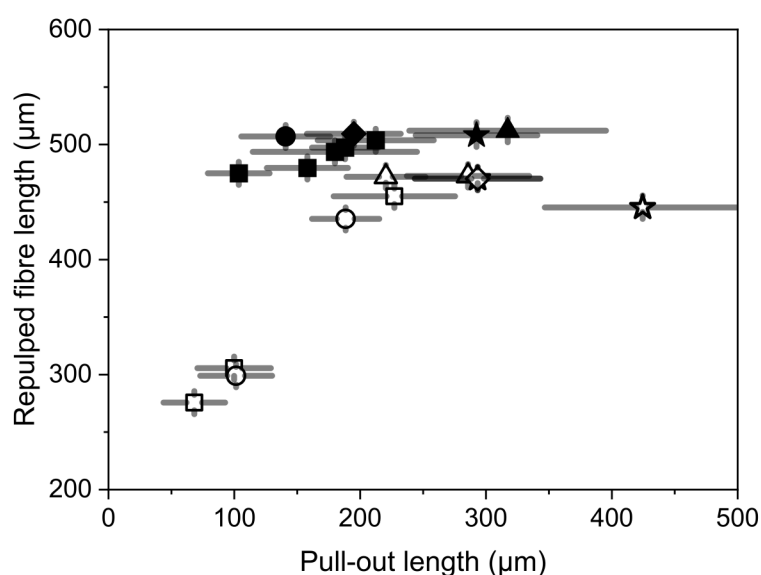
492 **Table 4:** Morphological parameters of the fibres and pulps as measured with MorFi: arithmetical mean length of
 493 fibres (standard deviation: $\Delta = 5 \mu\text{m}$), length of fine elements over the total length of detected objects ($\Delta = 2 \%$),
 494 percentage of kinked fibres ($\Delta = 0.4 \%$), for unaged paper and paper aged under humid air conditions.

Paper	Ageing (weeks)	DP_n	Length (μm)	Fine elements (%)	Kinked fibres (%)
Paper A	0	1870	508	37	14.8
	2	1348	504	41	15.0
	4	1281	497	41	14.5
	10	793	494	42	15.0
	25	476	480	41	14.2
	50	371	475	39	14.2
Paper B	0	358	445	29	16.1
	1	326	451	27	16.3
	2	159	455	25	17.0
	4	103	306	48	6.1
	10	88	276	61	3.8

495
 496 The evolution of the repulped fibre length upon ageing is presented **Table 4**. The ageing leads to a decrease of the
 497 fibre length in both papers. It is interesting to note that this diminution is significant for paper B after 4 weeks of
 498 ageing, considering the standard deviation of 5 μm , with the length decreasing by 38 % for 75 % decrease of DP_n ,
 499 compared to 6 % for paper A for 80 % decrease of DP_n . This degradation state corresponds to the reach of LODP,
 500 i.e., the chemical degradation state for which cellulose becomes less accessible, as observed in the case of the
 501 graphical representation of Page equation where a plateau is reached (section 3.2.2). A faster weakening of the
 502 fibres after LODP can explain the abrupt decrease of repulped fibre length between 2 and 4 weeks of ageing. The
 503 non-linearity observed after LODP implies that bLa parameter of Page equation can no longer be considered
 504 constant. It is also noteworthy that no specific behaviour related to the repulped fibre length can be observed at
 505 the DP_c of 750.

506 The abrupt change in average length in the case of paper B was related to other morphological parameters. **Table**
 507 **4** shows that this phenomenon is accompanied by an increase in the proportion of fine elements, and a drastic
 508 reduction of the percentage of kinked fibres. This evidences the fact that fibres break more easily, and the smaller
 509 parts of broken fibres no longer account as fibres but as fines. Moreover, the rupture of fibres most probably occurs
 510 at fibre kinks, explaining why the number of kinked fibres decrease. The production of fines from fibre breaks
 511 would only happen for a fraction of the broken fibres, justifying why the increase of the proportion of fines is
 512 lower than the decrease of kinked fibres. This seems to happen for DP_n lower than 100, and was thus not observed
 513 in the case of paper A.

514 Two phenomena can be put forward to explain specific breakage at kinks. On the one hand, if a kinked fibre is
 515 stressed at its extremities, the kink will be bent due to a localised concentration of stress (Aslan et al. 2011; Richely
 516 et al. 2022). This would lead to breaking at kinks. A homogenous chemical degradation along the fibre could
 517 thereupon lower the breaking criteria of kinks, allowing increasingly more fibre rupture during MorFi sample
 518 preparation, and thus a decrease of repulping fibre length. On the other hand, kinks are defects created in the fibres
 519 during the papermaking process. It can induce failures in both amorphous and crystalline zones (Ciesielski et al.
 520 2019), leading to less ordered cellulose. Chemically reactive sites could be more accessible to reactants, and thus
 521 more prone to degradation. More degradation in these areas would lead to less resistance of the fibres. This would
 522 mean that cellulose chains break at specific locations, leading to low and heterogenous chemical degradation. Even
 523 though possible, this was not observed for the papers tested (Vibert et al. 2023). Breakage at kinks is thus
 524 principally due to stress concentration, and the second phenomenon might happen to a lesser extent.



525

526 **Fig. 11:** Length of fibres measured in MorFi compared to the length of pulled-out fibres measured by
527 microscopy at fracture surface (initial values ★, humid air ■, humid nitrogen ●, dry air ▲, dry nitrogen ◆, full
528 symbols for paper A and empty symbols for paper B).

529 The fibre length obtained with MorFi analysis was compared to the length of the fibres at the fracture surface. The
530 results are presented on **Fig. 11**. For paper A, it shows that extracted lengths decrease more rapidly than repulped
531 fibre lengths. For paper B, the slope is constant only at low degradation levels after which it shows a linear
532 correlation for samples with DP below 250.

533 As already mentioned (section 3.3.1), the relationship between extracted length and fibre length could give insight
534 in the breaking mechanisms. On **Fig. 11**, the slope for paper A is 0.1, while the slope for paper B is close to zero
535 for low degradation levels and is 1.4 for higher degraded states. If we assume that the extraction length depends
536 on the fibre length, the correlation would be linear with a slope of 2. Indeed, for fibres that in average break in the
537 middle, when the fibre shortens by 1, the extracted length shortens by 0.5. Therefore, it can be concluded that the
538 evolution of the extracted length is not due to fibre shortening, but to a diminution of the fibre strength.

539 **4 Conclusions**

540 In conclusion, the results indicated that the embrittlement mechanism of paper was not affected by the exposure
541 conditions, since oxidative and hydrolytic exposure conditions lead to similar effects. The embrittlement process
542 is essentially driven by the reduction of degree of polymerisation by cellulose chain scissions.

543 The evolution of paper mechanical behaviour with ageing is primarily attributed to the embrittlement of the fibres
544 rather than to the fibre-fibre bonds modifications, as evidenced by the validity of Page equation. Testing the paper
545 in the transverse direction of the fibres allowed for the characterisation of the network by varying the ratio of fibres
546 to fibre-fibre bonds, which helped to confirm the first hypothesis.

547 A critical degree of polymerisation was identified around DP_n of 750 in the case of paper A, below which the
548 embrittlement occurs more significantly. The existence of this critical DP was confirmed by zero-span tensile tests,
549 indicating that the damage mechanism is localised in the fibre.

550 The fracture preferentially occurs at morphological defects along the fibres, as highlighted by MorFi measurements
551 for different states of paper degradation. This is not necessarily a symptom of heterogeneous degradation, but more
552 likely a concentration of stress at the kinks leading to early breakage in the conditions of the MorFi analysis.

553 **5 Statements & Declarations**

554 **Ethics approval and consent to participate**

555 Not applicable.

556 **Consent for publication**

557 All the authors give their consent for the publication of this manuscript.

558 **Availability of data and materials**

559 Data will be available upon reasonable request.

560 **Competing interests**

561 The authors have no relevant financial or non-financial interests to disclose.

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563 Not applicable.

564 **Authors' contribution**

565 Caroline Vibert: Conceptualization, Methodology, Investigation, Writing - Original Draft, Visualization; Anne-
566 Laurence Dupont: Resources, Writing - Review & Editing, Supervision, Project administration, Funding
567 acquisition; Justin Dirrenberger: Supervision, Funding acquisition; Raphael Passas: Resources, Data Curation,
568 Writing - Review & Editing; Denise Ricard: Resources, Funding acquisition; Bruno Fayolle: Writing - Review &
569 Editing, Supervision, Project administration, Funding acquisition.

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574

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738 **Supplementary Information**

739 The online version contains supplementary material: <https://doi.org/10.1007/s10570-023-05683-x>.